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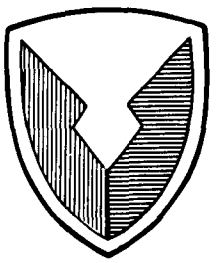

CCL REPORT NO. 155

NEW CORROSION INHIBITORS FOR ANTIFREEZES

BY

CHARLES B. JORDAN

AMCMS CODE NO. 5025.11.803
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16 JANUARY 1964

ABERDEEN PROVING GROUND
MARYLAND

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U.S. Army Coating and Chemical Laboratory
Aberdeen Proving Ground
Maryland

UNCLASSIFIED

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ABSTRACT

The object of this study was to conduct a preliminary investigation of newly developed corrosion inhibitors and inhibitor combinations for use in automotive coolants.

Bench corrosion tests were conducted on the following inhibitors in water and ethylene glycol/water solutions: sodium tetraborate/propylene glycol condensate, the double condensate of sodium tetraborate with propylene glycol and butynediol, and Specification 0-1-490 inhibitor modified by adding disodium phosphate and increasing the mercaptobenzothiazole content.

Many combinations of these inhibitors performed satisfactorily in the bench corrosion tests. Dynamometer tests and field tests are warranted.

I. INTRODUCTION

Aberdeen Proving Ground, Maryland, was authorized by AMC Program Directive, AMCMS Code 5025.11.803, dated 15 October 1962, to investigate improved antifreeze mixtures. One area being studied is the inhibitor system of Specification O-A-548a materials.

A sodium tetraborate/propylene glycol condensate (CCL Reports Numbers 76 and 86, U.S. Patent No. 3,087,959) and a newly developed double condensate of sodium tetraborate with propylene glycol and butynediol (CCL Report No. 113, patent pending) appeared to have application in antifreeze compounds. Also, a modification of the Specification O-I-490 Inhibitor, Corrosion Liquid Cooling System involving the addition of disodium phosphate was studied. Bench corrosion studies were conducted on these materials, with and without other additives, as a means of screening satisfactory combinations. Distilled water and a 50/50 (volume) mixture of ethylene glycol/water were used as the coolant media.

This report contains the results of this preliminary investigation.

II. DETAILS OF TEST

A. Bench Corrosion Tests

Bench corrosion tests were conducted in accordance with the procedure outlined in LSD Report No. 205, dated 26 February 1954. This procedure involves the immersion of a set of six metal test specimens (cast iron, aluminum, copper, brass, steel, solder) in a glass flask containing the test solution. The solution is aerated and refluxed at 180°F. for 192 hours, after which the metal test specimens are examined for evidence and extent of corrosion.

B. Test Solution

A 50/50 (volume) mixture of ethylene glycol/distilled water was used as the coolant medium. Comparative tests were conducted on distilled water.

C. Inhibitor Combinations

1. Sodium tetra borate/1,2-propylene glycol condensate - This material was developed (CCL Report No. 76) as a soluble corrosion inhibitor for brake fluids. Its chemical composition suggested a reserve alkalinity and potential solubility desirable in antifreeze solutions. It performed satisfactorily in storage tests with ethylene glycol mixtures (CCL Report No. 86). Quantities added are listed in Table I Appendix A.

2. Double condensate of sodium tetraborate with 1,2-propylene glycol and 2-butyne-1,4-diol - This material was developed as a single inhibitor for brake fluids (CCL Report No. 113). It possesses both alkalinity and antioxidant properties desirable in multi-metal systems, suggesting possible antifreeze application. Quantities added are listed in Table I, Appendix A.

3. Modified O-I-490 Inhibitor - This inhibitor has the following composition (weight):

Sodium tetraborate decahydrate	- 70.0%
Mercaptobenzothiazole (MBT)	- 14.0%
Disodium phosphate heptahydrate	- 16.0%

This material was developed because of the potential use of aluminum in cooling systems. O-I-490 inhibitor would not be completely satisfactory in some instances, such as would be encountered in vehicles with cast iron blocks and aluminum radiators. The phosphate is known to be a good inhibitor for both cast iron and aluminum. The increased amount of MBT provides a better coating on the metals and affords increased protection against erosion and corrosion attack. Quantities added are listed in Table I, Appendix A.

4. Additives - Many combinations were prepared by adding small percentages of sodium tetraborate, disodium phosphate, MBT, or sodium MBT to the basic inhibitor formulations under study.

D. Numerical Rating System

A numerical rating system has been devised (LSD Report No. 205) which allows a comparison of bench corrosion test results based on weight loss and visual evidence of corrosion of the metal strips. An arbitary value of 21 has been selected as the point of demarkation between satisfactory and unsatisfactory results. An overall value of 6 would indicate that each of the 6 metal test strips were perfect. Material supplied under O-A-548a, Type I and MIL-C-11755A usually rate about 16 - 18.

III. RESULTS OF TESTS

Results of tests are listed in Table I, Appendix A. Conclusions which can be drawn are as follows:

1. Ethylene glycol/water solution are easier to inhibit than water.
2. All inhibitor systems studied can be improved by the addition of MBT.
3. Most inhibitors modified with MBT can be further improved by disodium phosphate.
4. Both condensates and the modified O-I-490 are superior to O-I-490.
5. The single condensate appears useful and superior to the double condensate.
6. If these inhibitors are used, it may be possible to package glycol antifreezes containing MBT.

IV. RECOMMENDATIONS

It is recommended that further screening of these inhibitors be accomplished by dynamometer tests in simulated service circulating units. Should the simulated service tests prove satisfactory, field tests should be planned.

It is further recommended that findings in this report be considered in the revision of Specification O-I-490.

V. REFERENCES

1. Authority: AMC Program Directive, AMCMS Code 5025.11.803, dated 15 Oct 62.

2. Federal Specification O-A-548a, Antifreeze, Ethylene Glycol, Inhibited, dated 30 Dec 58.

3. Federal Specification O-I-490, Inhibitor, Corrosion, Liquid Cooling System, dated 27 Nov 57.

4. Military Specification, MIL-C-11755A, Compound, Antifreeze, Arctic Type, dated 17 July 59.

5. LSD Report No. 205, Development of a Suitable Laboratory Bench Corrosion Test for Antifreeze Compounds and Inhibitors, dated 26 Feb 54.

6. CCL Report No. 76, A Review of the Use of Sodium Tetraborate as a Corrosion Inhibitor for Hydraulic Brake Fluids, dated 6 May 59.

7. CCL Report No. 86, Effects of Inhibited Ethylene Glycol on Tin Coated Steel Containers, dated 28 Dec 59.

8. CCL Report No. 113, Improved Multipurpose Corrosion Inhibitor, dated 15 Jan 62.

9. U.S. Patent No. 3,087,959, Soluble Borax Inhibitor, dated 30 April 63.

APPENDIX A

Table I

TABLE I

RESULTS OF BENCH CORROSION TESTS

Test Number	1		2		3	
Coolant	50/50 ethylene glycol/water		50/50 ethylene glycol/water		50/50 ethylene glycol/water	
Inhibitor	7.0% single condensate		7.0% single condensate 1.0% borax		7.0% single condensate 0.96% borax 0.08% sodium MBT	
pH Before	7.34		7.38		7.40	
pH After	7.35		7.35		7.40	
RA Before	8.80		14.00		14.30	
RA After	8.60		13.70		13.95	
Results	Wt loss mg/sq cm	Visual	Wt loss mg/sq cm	Visual	Wt loss mg/sq cm	Visual
Aluminum	.04	Stain	.05	Stain	.15	Stain
Copper	+ .01	Stain	+.02	Very slight stain	.00	Very slight stain
Solder	.26	OK	.11	OK	.02	OK
Brass	+ .01	Very slight stain	+ .01	Very slight stain	+ .02	Very slight stain
Steel	.00	OK	.01	OK	.01	OK
Cast Iron	.00	OK	.07	OK	.01	OK
Remarks						
C&CL Rating	11/11		110/10		110/10	

TABLE I

RESULTS OF BENCH CORROSION TESTS (CONTINUED)

Test Number	4		5		6	
Coolant	50/50 ethylene glycol/water		50/50 ethylene glycol/water		50/50 ethylene glycol/water	
Inhibitor	7.0% single condensate 1.0% 0-1-490		7.0% single condensate 0.08% sodium MBT		7.0% single condensate 0.06% disodium phosphate	
pH Before	7.38		7.38		7.35	
pH After	7.38		7.38		7.30	
RA Before	15.00		9.10		10.75	
RA After	14.80		9.10		10.45	
Results	Wt loss mg/sq cm	Visual	Wt loss mg/sq cm	Visual	Wt loss mg/sq cm	Visual
Aluminum	.15	Stain	.13	Stain	.00	OK
Copper	+.06	Stain	+.03	Very slight stain	+.01	Slight stain
Solder	.05	OK	.02	OK	15.09	Very slight stain
Brass	+.07	Very slight stain	+.04	Very slight stain	.00	Very slight stain
Steel	.00	OK	.04	Stain at contact	.00	OK
Cast Iron	.01	OK	.14	Stain at contact	.00	Stain
Remarks						
C&CL Rating	9/10		10/11		19/18	

TABLE I

RESULTS OF BENCH CORROSION TESTS (CONTINUED)

Test Number	7		8		9	
Coolant	50/50 ethylene glycol/water		100% water (distilled		50/50 ethylene glycol/water	
Inhibitor	7.0% single condensate 1.0% modified 0-1-490		7.0% single condensate		7.0% double condensate	
pH Before	7.35		8.58		7.32	
pH After	7.30		8.58		7.20	
RA Before	14.75		8.80		8.00	
RA After	14.20		8.60		6.50	
Results	Wt loss mg/sq cm	Visual	Wt loss mg/sq cm	Visual	Wt loss mg/sq cm	Visual
Aluminum	.00	OK	3.70	Stain	.03	Stain
Copper	+.01	Very slight stain	+.08	Stain	2.09	Stain
Solder	.02	OK	.00	Slight stain	2.48	Slight pitting
Brass	+.01	Very slight stain	+.15	Stain	.01	Slight stain
Steel	.00	OK	+.14	Stain	.61	Slight stain
Cast Iron	+.01	OK	+.20	Stain	1.68	Slight stain
Remarks					Unsatisfactory	
C&CL Rating	8/8		19/19		35/33	

TABLE I

RESULTS OF BENCH CORROSION TESTS (CONTINUED)

Test Number	10		11		12	
Coolant	50/50 ethylene glycol/water		50/50 ethylene glycol/water		50/50 ethylene glycol/water	
Inhibitor	7.0% double condensate 1.0% borax		7.0% double condensate 0.96% borax 0.08% sodium MBT		7.0% double condensate 1.0% O-I-490	
pH Before	7.38		7.32		7.32	
pH After	7.35		7.32		7.32	
RA Before	12.60		13.10		14.30	
RA After	11.50		12.60		13.80	
Results	Wt loss mg/sq cm	Visual	Wt loss mg/sq cm	Visual	Wt loss mg/sq cm	Visual
Aluminum	.00	Slight stain	.00	Stain	.10	Stain
Copper	2.54	Stain	.00	Very slight stain	+.01	Stain
Solder	3.53	Pitting	+.03	OK	.00	OK
Brass	.12	Stain	+.02	Very slight stain	+.01	Very slight stain
Steel	.00	Very slight stain	+.02	OK	+.01	OK
Cast Iron	+.02	Slight stain	+.01	OK	.00	OK
Remarks	Unsatisfactory					
C&CL Rating	26/27		9/9		9/9	

TABLE I

RESULTS OF BENCH CORROSION TESTS (CONTINUED)

Test Number	13		14		15	
Coolant	50/50 ethylene glycol/water		50/50 ethylene glycol/water		50/50 ethylene glycol/water	
Inhibitor	7.0% double condensate 0.08% sodium MBT		7.0% double condensate 0.06% disodium phosphate		7.0% double condensate 1.0% modified O-I-490	
pH Before	7.38		7.40		7.40	
pH After	7.38		7.40		7.40	
RA Before	8.10		9.00		13.30	
RA After	7.90		8.60		12.90	
Results	Wt loss mg/sq cm	Visual	Wt loss mg/sq cm	Visual	Wt loss mg sq cm	Visual
Aluminum	.00	Very slight stain	.00	OK	+ .01	OK
Copper	+ .01	Very slight stain	.01	Very slight stain	.00	Very slight stain
Solder	.00	OK	6.03	Etched	+ .01	OK
Brass	.00	Very slight stain	.00	Very slight stain	+ .01	Very slight stain
Steel	+ .01	OK	.00	OK	+ .02	OK
Cast Iron	+ .01	OK	.00	Very slight stain	.00	OK
Remarks						
C&CL Rating	12/9		17/18		9/8	

TABLE I

RESULTS OF BENCH CORROSION TESTS (CONTINUED)

Test Number	16		17		18	
Coolant	50/50 ethylene glycol/water		100% water (distilled)		50/50 ethylene glycol/water	
Inhibitor	1.0% double condensate 1.0% modified O-I-490		7.0% double condensate		1.0% modified O-I-490	
pH Before	7.40		8.53		7.37	
pH After	7.25		8.52		7.30	
RA Before	6.00		8.30		4.13	
RA After	5.51		7.80		4.39	
Results	Wt loss mg/sq cm	Visual	Wt loss mg/sq cm	Visual	Wt loss mg/sq cm	Visual
Aluminum	.02	OK	2.96	Stain	.01	OK
Copper	+ .04	Very slight stain	.86	Stain	.00	OK
Solder	+ .29	Slight stain	+ .02	Very slight stain	.05	OK
Brass	+ .05	Slight stain	.05	Slight stain	.00	OK
Steel	+ .02	OK	+ .02	Stain	.00	OK
Cast Iron	.05	OK	+ .07	Stain	.02	OK
Remarks			Unsatisfactory			
C&CL Rating	9/9		23/23		7/6	

TABLE I

RESULTS OF BENCH CORROSION TESTS (CONTINUED)

Test Number	19		20		21	
Coolant	100% water (distilled)		50/50 ethylene glycol/water		100% water (distilled)	
Inhibitor	1.32% modified O-I-490		1.0% O-I-490		1.5% O-I-490	
pH Before	8.92		7.42		9.10	
pH After	8.82		7.39		9.08	
RA Before	5.80		6.55		9.00	
RA After	5.80		6.75		9.00	
Results	Wt loss mg/sq cm	Visual	Wt loss mg/sq cm	Visual	Wt loss mg/sq cm	Visual
Aluminum	1.20	Stain	.02	Stain	8.01	Pitting
Copper	+ .02	Stain	.00	Slight stain	+.13	Stain
Solder	.13	Stain	.06	OK	.62	Stain
Brass	+.05	Slight stain	+.03	Slight stain	+.19	Very slight stain
Steel	.01	Slight stain	.03	Stain at contact	+.20	Slight stain
Cast Iron	.01	Slight stain	.02	Stain at contact	+.20	Slight stain
Remarks					Unsatisfactory	
C&CL Rating	19/19		11/12		25/25	

TABLE I

RESULTS OF BENCH CORROSION TESTS (CONTINUED)

Test Number	22		23		24	
Coolant	50/50 ethylene glycol/water		100% water (distilled)		100% water (distilled)	
Inhibitor	1.25% borax		1.25% borax		none	
pH Before	7.40		9.10		5.58	
pH After	7.40		9.15		7.52	
RA Before	6.60		6.50		0.00	
RA After	6.50		6.75		0.10	
Results	Wt loss mg/sq cm	Visual	Wt loss mg/sq cm	Visual	Wt loss mg/sq cm	Visual
Aluminum	.00	OK	6.56	Etching stain	.33	Stain
Copper	.09	Stain	.02	Stain	.00	Slight stain
Solder	.55	Very slight etching	.84	Etching	.12	Stain
Brass	.01	Very slight stain	+.09	Stain	+ .03	Slight stain
Steel	.29	Very slight stain	+.14	Stain	8.45	Pitting
Cast Iron	.43	Very slight stain	+.14	Stain	16.02	Pitting
Remarks	Borderline		Unsatisfactory		Unsatisfactory	
C&CL Rating	22/21		24/25		33/32	

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